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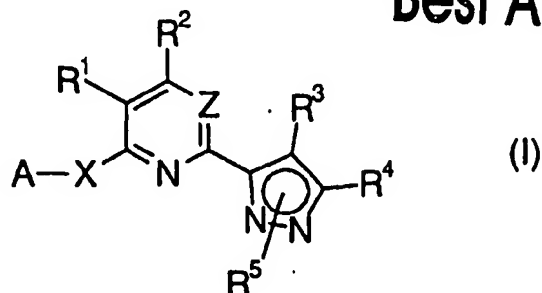
(71) Applicant: **BASF AKTIENGESELLSCHAFT**
67056 Ludwigshafen (DE)

(72) Inventors:
 • Kleemann, Axel, Dr.
 61462 Königstein (DE)
 • Maler, Thomas, Dr.
 78333 Stockach (DE)

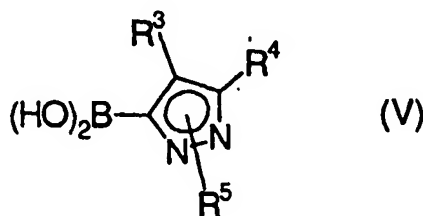
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(54) **Herbicidal 2-Pyrazolyl-6-Aryloxy-Pyri(mi)dines**

(57) The invention relates to novel compounds of formula I:



wherein R¹ through R⁵, A, X and Z have the meaning set forth in the description. Furthermore the invention relates to a process for the preparation of the novel compounds of formula I, to a novel pyrazol-5-ylboronic acid of formula V, which is used in said process



wherein R³ through R⁵ have the meaning set forth in the description and to a herbicidal composition containing such compounds as active ingredients

Description

[0001] This invention relates to certain novel 2-pyrazolyl-6-aryloxy-pyri(mi)dines, to the preparation of such compounds, to certain novel intermediates, to herbicidal compositions containing such compounds, and to a method of combating undesired plant growth using such compounds.

[0002] Pyridines, pyrimidines and their derivatives have many uses in the pharmaceutical area as well as in agriculture (herbicides, fungicides, acaricides, anthelmintics, bird repellents), as reagents, intermediates and chemicals for the polymer and textile industry.

[0003] The US patent US 5,750,470 discloses 2-azol-2-yl-5-aryloxy-pyridines in which the azolyl moiety contains at least two heteroatoms in the 1- and 3-position.

[0004] Similar 2-phenyl-6-aryloxy-pyri(mi)dines are disclosed by EP 0 723 960.

[0005] The broad generic formula of the International patent application WO 98/21199 embraces 2-pyrazol-5-yl-6-phenyloxy-pyridines, in which a hydrogen or halogen atom or a methyl group is attached in the 3-position of the pyridine ring.

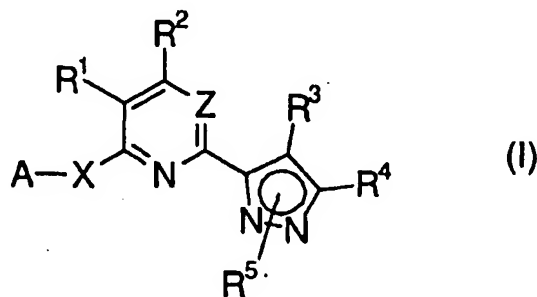
[0006] The broad generic formula of the International patent application WO 98/56789 embraces 2-heteroar-2-yl-4-aryloxy-pyrimidines in which the heteroaryl moiety is a 5-membered ring containing at least one heteroatoms in the 1-position.

[0007] However, none of these documents discloses 2-pyrazol-5-yl-6-hetero-aryloxy-pyridines nor 2-pyrazol-5-yl-6-(hetero)aryloxy-pyri(mi)dines.

[0008] Although many of the known compounds show considerable activity against various weeds, they are not completely satisfying with regard to their selectivity or because of their persistence.

[0009] The compounds according to the present invention combine high herbicidal activity with good selectivity and a desirable rate of degradation in soil.

[0010] The present invention provides novel compounds of the general formula I



wherein

[0011] A represents an optionally substituted aryl group or an optionally substituted 5- or 6-membered nitrogen- or sulfur-containing heteroaromatic group or a difluorobenzodioxolyl group;

Z represents N or CR⁶;

X represents -O-, -S-, -CH₂O- or -CH₂S-;

R¹ and R² each independently represent a hydrogen or halogen atom, or an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy group, or a haloalkyl, haloalkoxy, cyano, nitro group; or -S(O)_n-R⁷, in which n is 0, 1 or 2, and R⁷ represents an alkyl or haloalkyl group; or -NR⁸R⁹, in which R⁸ and R⁹ each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group, or R¹⁰O-CY-, in which R¹⁰ represents an alkyl group, and Y represents O or S;

R³ represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, haloalkyl, cyano or nitro group, or -NR¹¹R¹², in which R¹¹ and R¹² each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group,

R⁴ represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy, haloalkyl,

haloalkoxy, cyano, nitro group, or $-S(O)_m-R^{13}$, in which m is 0, 1 or 2, and R^{13} represents an alkyl or haloalkyl group; and

R^5 represents a hydrogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, cycloalkyl, haloalkyl, haloalkenyl, cyanoalkyl or cyano group;

or an agriculturally acceptable salt or N-oxide thereof; with the proviso that

a) R^1 and R^6 both represent a hydrogen atom, and/or

b) R^2 represents a halogen atom, or an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy group, or a haloalkyl, haloalkoxy, cyano, nitro group; or $-S(O)_n-R^7$, in which n is 0, 1 or 2, and R^7 represents an alkyl or haloalkyl group; or $-NR^8R^9$, in which R^8 and R^9 each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group, or $R^{10}O-CY-$, in which R^{10} represents an alkyl group, and Y represents O or S;

In the event that Z represents CR^6 and A represents an optionally substituted aryl group or an optionally substituted 6-membered nitrogen- or sulfur-containing heteroaromatic group.

[0012] The new compounds show an excellent selective herbicidal activity in certain crops, such as maize and rice, and degrade well in soil.

[0013] It is an object of the present invention to provide novel herbicidal compounds.

[0014] It is another object of the invention to provide methods for controlling undesired plant growth by contacting said plants with a herbicidally effective amount of the new compounds.

[0015] It is another object of the invention to provide selective herbicidal compositions containing the new compounds as active ingredients.

[0016] It is another object of the invention to provide new processes for the preparation of the new compounds.

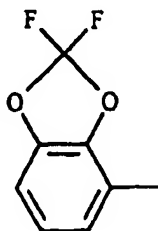
[0017] These and other objects and features of the invention will become more apparent from the detailed description set forth hereinbelow.

[0018] It has surprisingly been found that the novel compounds of formula I, in which R^1 through R^5 , A, X, and Z have the meaning given above, show excellent herbicidal activity against a broad range of weeds.

[0019] The expression "pyr(mi)dine" as used hereinbefore or hereinbelow includes both pyridine and pyrimidine moieties. The expression "azoly" as used hereinbefore or hereinbelow includes 5-membered heteroaryl groups containing at least one nitrogen atom.

[0020] An aryl group as substituent or part of other substituents or in the definition of A is suitably an optionally substituted phenyl group. Within the definition of A the 5- or 6-membered heteroaryl group comprises optionally substituted 5- or 6-membered heterocycles containing one or more nitrogen and/or oxygen and/or sulfur atoms, 1 to 3 nitrogen atoms being preferred. Examples of such groups are pyrazolyl, imidazolyl, triazolyl, tetrazolyl, thienyl, pyridyl, pyrazinyl, pyrimidyl, pyridazinyl, isoxazolyl, isothiazolyl and triazinyl groups. As far as A is concerned, the definition "aryl" also includes bicyclic systems which consist of a benzene ring fused with a 5- or 6-membered heterocyclic ring as defined above and in turn the 5- or 6-membered heterocycles may be fused with a benzene ring.

[0021] One especially preferred embodiment of the invention is a compound in which A is a difluorobenzodioxolyl group of formula



[0022] A preferably represents a phenyl, pyridyl, thienyl or pyrazolyl group being substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups and SF_5 groups, and preferably has a substituent in the meta-position relative to the point of attachment; more preferably A is meta-substituted by a fluorine or chlorine atom, or a trifluoromethyl, trifluoromethoxy or difluoromethoxy group. If A represents a thienyl group, it may be attached

In the 2- or 3-position with respect to the sulfur atom, 3-thienyl groups are preferred.

[0023] Generally, if any of the above mentioned moieties comprises an alkyl, alkenyl or alkynyl group, such groups, unless otherwise specified, may be linear or branched and may contain 1 to 6, preferably 1 to 4, carbon atoms. Examples of such groups are methyl, ethyl, propyl, vinyl, allyl, propargyl, isopropyl, butyl, isobutyl and tertiary-butyl groups. The alkyl portion of a haloalkyl, haloalkoxy, haloalkylthio, alkylthio or alkoxy group suitably has from 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms. The number of carbon atoms in the alkoxyalkyl, alkoxyalkoxy or dialkoxyalkyl groups is up to 6, preferably up to 4, e.g. methoxymethyl, methoxymethoxy, methoxyethyl, ethoxymethyl, ethoxyethoxy, dimethoxymethyl.

[0024] "Halogen" means a fluorine, chlorine, bromine or iodine atom, preferably fluorine, chlorine or bromine. Haloalkyl moieties of any groups within the definitions used herein and as such can contain one or more halogen atoms. Haloalkyl, haloalkoxy and haloalkylthio are preferably mono-, di-, tri- or perfluoroalkyl, -alkoxy and -alkylthio, especially trifluoromethyl, pentafluoroethyl, trifluoromethoxy, difluoromethoxy, difluoromethylthio, tri-fluoromethylthio or 2,2,2-trifluoroethoxy groups.

[0025] When any groups are designated as being optionally substituted, the optional substituent groups may be any of those customarily employed in the modification and/or development of pesticidal compounds and are especially substituents that maintain or enhance the herbicidal activity associated with the compounds of the present invention, or influence persistence of action, soil or plant penetration, or any other desirable property of such herbicidal compounds.

[0026] There may be one or more of the same or different substituents present in each part of the molecules. In relation to moieties defined above as comprising an optionally substituted alkyl group, including alkyl parts of haloalkyl, alkoxy, alkylthio, haloalkoxy, alkylamino and dialkylamino groups, specific examples of such substituents include phenyl, halogen atoms, nitro, cyano, hydroxyl, C₁₋₄-alkoxy, C₁₋₄-haloalkoxy and C₁₋₄-alkoxycarbonyl groups.

[0027] In relation to moieties defined above as comprising an optionally substituted aryl or heteroaryl group, optional substituents include halogen, especially fluorine, chlorine and bromine atoms, and nitro, cyano, amino, hydroxy, phenoxy, C₁₋₄-alkyl, C₁₋₄-alkoxy, C₁₋₄-haloalkyl, C₁₋₄-haloalkenyl, C₁₋₄-haloalkoxy, C₁₋₄-haloalkylthio, C₁₋₄-alkylsulfonyl and halosulfanyl groups such as SF₅. In the case of phenyl-groups 1 to 5 substituents may suitably be employed, in the case of thienyl-groups 1 to 3 substituents may suitably be employed, 1 or 2 substituents being preferred.

[0028] One skilled in the art will appreciate that not all nitrogen containing heterocycles can form N-oxides; one skilled in the art will recognize those nitrogen atoms which can form N-oxides. Synthetic methods for the preparation of N-oxides of heterocycles are very well known by one skilled in the art including the oxidation of heterocycles with peroxy acids such as peracetic acid and m-chloroperoxybenzoic acid (MCPBA), hydrogen peroxide, alkylhydroperoxides such as tert-butyl hydroperoxide. Such methods for the preparation of N-oxides have been described and reviewed in the literature, as for example: T.L. Gilchrist in *Comprehensive Organic Synthesis*, vol. 7, pp 748-750 and in *Advances in Heterocyclic Chemistry*, vol. 9, pp 285-291, vol. 22, pp 390-392 and vol. 43, pp 149-161, A.R. Katritzky, Ed., Academic Press.

[0029] Compounds of the invention include compounds of formula I, isotopes thereof, geometric and stereoisomers thereof, N-oxides thereof, and agriculturally suitable salts thereof. The compounds of the invention can exist as one or more stereoisomers. The various isotopes include compounds of formula I, in which at least one natural occurring isotope such as a hydrogen or ¹²C carbon atom is replaced by another isotope thereof such as deuterium or ¹³C. The various stereoisomers include enantiomers, diastereomers, atropi-somers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or selectively prepare said stereoisomers. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

[0030] The salts of the compounds of the invention include acid-addition salts of inorganic and organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, oxalic, propionic salicylic, tartaric, toluenesulfonic or valeric acids.

[0031] Preferred compounds of the invention for reasons of better activity and/or ease of manufacture or handling are:

a) Compounds of formula I, wherein Z represents CR⁶, and A represents an optionally substituted 5-membered nitrogen and/or sulphur containing heteroaromatic group.

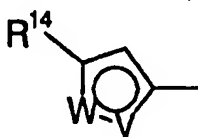
b) Compounds of formula I, wherein Z represents CR⁶, and R² represents a halogen atom, or an optionally substituted alkyl or alkoxy group, or a cyano group, or -NR⁸R⁹, in which R⁸ and R⁹ each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group.

c) Compounds of formula I, wherein R³ represents a hydrogen atom, R⁴ represents a halogen atom, or an alkyl, haloalkyl or haloalkoxy group, and R⁵ represents a hydrogen atom, or an alkyl group.

d) Compounds of formula I, wherein X is oxygen.

e) Compounds of formula I, wherein A represents a phenyl, pyridyl, pyrazolyl or thienyl group, substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups.

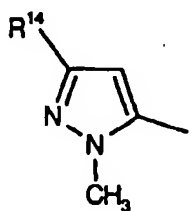
f) Compounds of formula I, wherein A is a group of formula



wherein

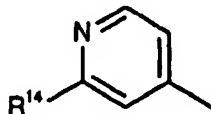
R^{14} represents a halogen atom or a haloalkyl or haloalkoxy group;

$W-V$ represents $N-CH$, $S-CH$, $N-CH-CH$, $CH-CH-CH$ or $N-N(CH_3)$, in particular wherein A represents a group of formula a, b, c or d:



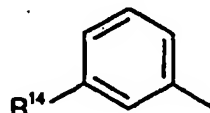
(a)

or



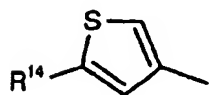
(b)

or



(c)

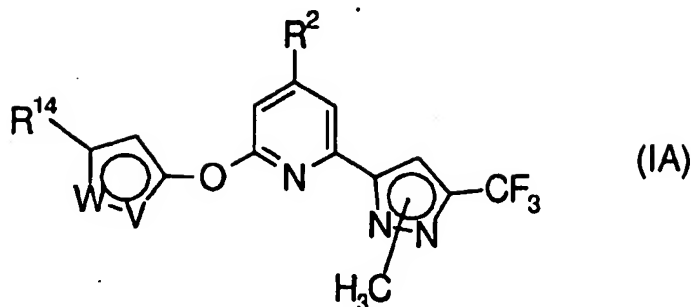
or



(d)

wherein R^{14} is a halogen atom or a C_{1-3} haloalkyl or C_{1-3} haloalkoxy group, most preferred a chlorine atom, or a trifluoromethyl, pentafluoroethyl, trifluoromethoxy or difluoromethoxy group. Most preferably A represents a group of formula (a).

[0032] Particularly preferred are the compounds of formula IA:



15 wherein

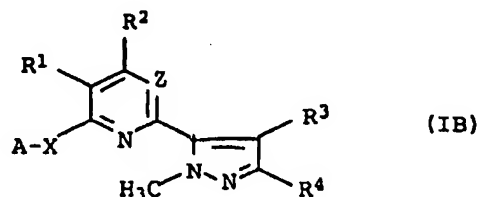
R² represents a hydrogen atom or an alkyl or cyano group;

R¹⁴ represents a halogen atom or a haloalkyl or haloalkoxy group;

W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-N(CH₃), in particular N-N(CH₃).

[0033] Preferably, R² represents an C₁₋₈ alkyl group, in particular a methyl or ethyl group.

g) Compounds of formula IB



Especially compounds IB, wherein R¹ is hydrogen. Particularly preferred are compound IB, wherein R¹ and R³ are hydrogen, in particular wherein R⁴ is trifluoromethyl; Also preferred are compounds IB wherein A is an optionally substituted 5-membered nitrogen- or sulfur-containing heteroaromatic group;

[0034] Also preferred are compound IB wherein A represents an optionally substituted aryl group or an optionally substituted 6-membered nitrogen- or sulfur-containing heteroaromatic group.

[0035] The invention is exemplified by the following specific compounds:

2-(2,4-difluorobenzoyloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(2-chloropyrid-4-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(3-chloropyrid-5-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(3-chloropyrid-5-yl-oxy)-6-(2'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(2'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-4-methyl-pyridine, 2-(3-trifluoromethylphenoxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-4-methylpyridine, 2-(benzyl-oxy)-4-cyano-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine, 4-cyano-2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine and 4-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-2-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-5-methylpyrimidine.

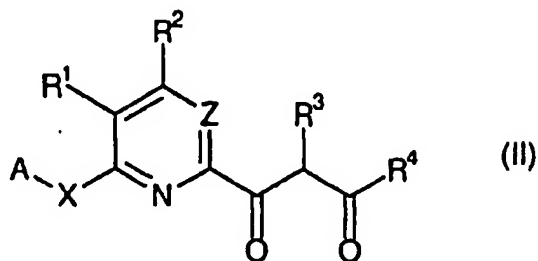
[0036] The compounds of this invention may be oils, gums, or crystalline solid materials. They can be used in agriculture or related fields for the control of undesired plants. The compounds of general formula I according to the invention possess a high herbicidal activity within a wide concentration range and at low dosages, and may readily be used in agriculture, especially for the selective control of undesired plants such as *Alopecurus myosuroides*, *Echinochloa crus-galli*, *Setaria viridis*, *Galium aparine*, *Stellaria media*, *Veronica persica*, *Lamium purpureum*, *Viola arvensis*, *Abutilon theophrasti*, *Ipomoea purpurea* and *Amaranthus retroflexus* by pre- and post-emergence application, and particularly in certain crops, such as maize and rice.

[0037] The compounds according to the invention can be prepared by conventional methods, particularly as follows:

EP 1 108 720 A1

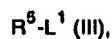
(A) A suitable process for the preparation of the compounds of formula I comprises the steps of:

(a) reacting a respective compound of the general formula II,



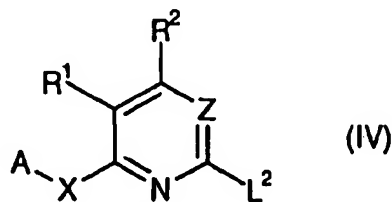
in which A, R¹, R², R³, R⁴, X and Z have the same meaning as in formula I, with hydrazine or an alkylhydrazine to obtain a compound of formula I, wherein R⁵ represents a hydrogen atom or an alkyl group, and

20 (b) optionally reacting the resulting compound with a compound of formula III,



25 in which R⁵ has the same meaning as in Formula I, and L¹ represents a suitable leaving group, optionally in the presence of a base.

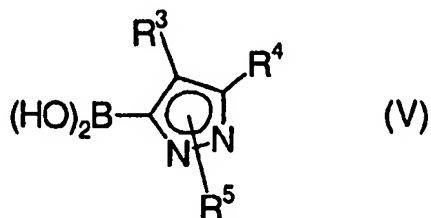
(B) Alternatively a compound of formula IV:



40 In which

A, R¹, R², X and Z have the same meaning as in formula I, and

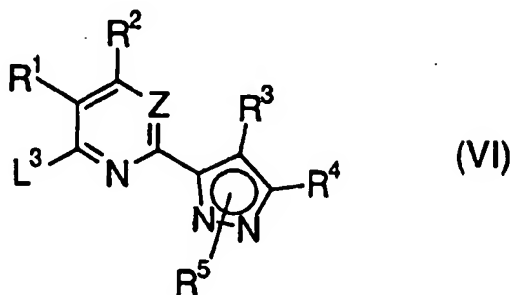
45 L¹ represents a suitable leaving group, with a pyrazol-5-ylboronic acid of formula V



In which

R³, R⁴ and R⁵ have the same meaning as in Formula I, in the presence of a transition metal and optionally a base.

(C) Alternatively a compound of formula VI:



In which

R¹ through R⁵ and Z have the same meaning as in formula I, and

L³ represents a suitable leaving group, can be reacted with a compound of formula VII or a metal salt thereof



(VII)

In which

A and X have the same meaning as in formula I, optionally in the presence of a base.

[0038] The compounds of formula VI can be obtained analogously to Method (A).

[0039] The cross coupling reaction (B) generally may be carried out in the presence of a transition metal complex, as for example described in Tetrahedron 48 (1992) 8117, and Chem. Scr. 26 (1986) 305. Preferred transition metals are Pd or Ni. Compounds of general formula V may be prepared and isolated separately or may be prepared in situ.

[0040] The reactions according to (A), (B) or (C) may be carried out in the absence or presence of a solvent which promotes the reaction or at least does not interfere with it. Preferred are polar, aprotic or protic solvents, suitably being N,N-dimethylformamide, dimethylsulfoxide, sulfolane, acetonitrile, methyl ethyl ketone, or an ether, such as tetrahydrofuran or dioxane, or alcohols, or water, or mixtures thereof. The reactions are carried out at a temperature between ambient temperature and the reflux temperature of the reaction mixture, preferably at elevated temperature, especially at reflux temperature.

[0041] The reactions may be carried out in the presence of a base such as an alkali hydroxide, bicarbonate or carbonate, e. g. sodium or potassium hydroxide, bicarbonate or carbonate, an alkali alkoxide, e. g. sodium ethoxide, or an organic base such as triethylamine.

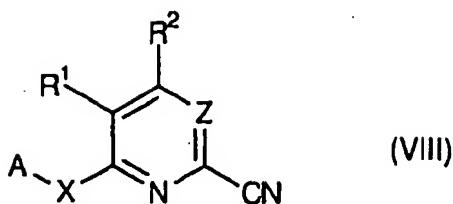
[0042] A hydroxy or thio compound used in the above reactions may be present in form of a salt, preferably as a salt of an alkali metal, particularly of sodium or potassium. The presence of a copper salt may be suitable.

[0043] Suitable leaving groups L¹, L² and L³ are each independently e.g. alkyl- and arylsulfonyl groups, alkyl- and arylsulfonyloxy, per-fluoroalkylsulfonyloxy groups, and halogen atoms, particularly methylsulfonyl, p-toluenesulfonyl and trifluoromethylsulfonyl groups or fluorine, chlorine and bromine atoms.

[0044] For compounds of formula I, II, IV or VI, certain substituents R¹ and R² like alkyl, alkoxy, alkylthio, alkylamino, dialkylamino, amino or halo, can be introduced onto the pyridine or pyrimidine ring by displacement of a alkyl- or arylsulfonyl, alkyl- or aryl-sulfonyloxy group, or halogen atom, or of a aryl- or heteroalkoxy group like A-O group, wherein A has the meaning given. Halogen atoms may also be introduced by diazotization of an amino group.

[0045] The compounds used as starting material are partly known and partly novel. The invention relates to the novel intermediates, in particular to the compounds of formula V, which can be prepared analogously to known methods.

[0046] Intermediates of formula II can be obtained by the reaction the corresponding cyano compounds of formula VIII



10 with a compound of formula IX

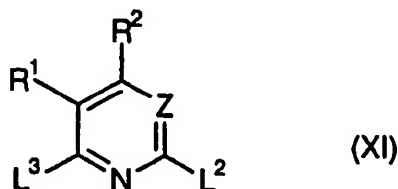


in which R¹ through R³, X and A are as described hereinabove, and Met represents a metal atom such as lithium, sodium or potassium or a group of formula MgHal with Hal being a halogen atom and treatment of the resulting ketone with an ester of formula X



in which R⁴ is as described hereinabove, and R' represents an alkyl group, in the presence of a strong base.

25 [0047] Intermediates of formula IV and VI can suitably be prepared starting from compounds of formula XI,



35 in which R¹, R², L², L³ and Z have the meaning given above, by conventional methods known in pyridine chemistry, as described in G.R.Newkome, "Pyridine and its Derivatives", in The Chemistry of Heterocyclic Compounds, Vol.14, Part 5, Eds. A. Weissberger and E.C. Taylor, John Wiley & Sons, New York - Chichester - Brisbane - Toronto - Singapore 1984.

40 [0048] For the preparation of the intermediates of formula IV the compound of formula XI is reacted with a compound of formula V essentially under the same conditions given for method (B).

45 [0049] The present invention also provides the use of the compounds of formula I as herbicides. Further, in accordance with the invention there is provided a method of combating undesired plant growth at a locus by treating the locus with a composition according to the invention or an effective amount of a compound of formula I. As a useful action is by foliar spray application, the locus is most suitably the plants in a crop area, typical crops being cereals, maize, soya bean, sunflower or cotton. However, application may also be to the soil for those compounds having pre-emergence herbicidal action, or to the water of paddy rice fields. The dosage of active ingredient used may, for example be in the range of from 0.005 to 3 kg/ha, preferably 0.01 to 1 kg/ha.

50 [0050] The compounds of general formula I have been found to show interesting activity as herbicides. Accordingly, the invention further provides a herbicidal composition comprising a compound of formula I as defined above in association with at least one carrier, and a method of making such a composition which comprises bringing a compound of formula I into association with at least one carrier. Preferably, there are at least two carriers, at least one of which is a surface-active agent.

55 [0051] The invention also provides a method of combating undesired plant growth at a locus, comprising application of such a compound or composition.

[0052] Particularly interesting activity has been found against grasses and broad leaf weeds, pre- and post-emergence. Selectivity in important crop species such as wheat, barley, maize, rice and soya-beans has also been found.

This activity provides a further aspect of the present invention.

[0053] In a method as mentioned above, the dosage of the active ingredient, the compound of general formula I, may, for example, be from 0.005 to 10 kg/ha, suitably 0.01 to 4 kg/ha. The locus may be an agricultural or horticultural locus, comprising, for example, a plant or soil. In a preferred method the locus contains undesired plant growth and treatment is by foliar spray application.

[0054] The invention also provides the use of a compound as defined above, as a herbicide. The compounds of general formula I have been found to have herbicidal activity. Accordingly, the invention further provides a herbicidal composition which comprises an active ingredient, which is at least one compound of formula I as defined above, and one or more carriers. A method of making such a composition is also provided which comprises bringing a compound of formula I as defined above into association with the carrier(s). Such a composition may contain a single active ingredient or a mixture of several active ingredients of the present invention. It is also envisaged that different isomers or mixtures of isomers may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

[0055] A composition according to the invention preferably contains from 0.5% to 95% by weight (w/w) of active ingredient.

[0056] A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

[0057] The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules, gels and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

[0058] Solvents may be aromatic hydrocarbons, e.g. Solvesso® 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or γ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different liquids are often suitable.

[0059] Solid carriers, which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand. Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

[0060] Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain at two or more carriers, at least one of which is a surfactant.

[0061] Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of individual surfactants.

[0062] The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually milled so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v

of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.

[0063] Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

[0064] Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be protected as disclosed for example by U.S. patent no. 5,705,174.

[0065] The biological activity of the active ingredient can also be increased by including an adjuvant in the spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

[0066] As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient. The doses usually are in the range from 0.01 to 10 kg a.i./ha.

[0067] Examples of formulations according to the invention are:

Emulsion Concentrate (EC)		
Active Ingredient	Compound of Example 5	30 % (w/v)
Emulsifier(S)	Atlox® 4856 B / Atlox® 4858 B ¹⁾ (mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics / mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics)	5 % (w/v)
Solvent	Shellisol® A ²⁾ (mixture of C ₉ - C ₁₀ aromatic hydrocarbons)	to 1000 ml
Suspension Concentrate (SC)		
Active Ingredient	Compound of Example 5	50 % (w/v)
Dispersing agent	Soprophor® FL ³⁾ (polyoxyethylene polyaryl phenyl ether phosphate amine salt)	3 % (w/v)
Antifoaming agent	Rhodorsil® 422 ³⁾ (nonionic aqueous emulsion of polydimethylsiloxanes)	0.2 % (w/v)
Structure agent	Kelzan® S ⁴⁾ (Xanthan gum)	0.2 % (w/v)
Antifreezing agent	Propylene glycol	5 % (w/v)
Biocidal agent	proxo® ⁵⁾ (aqueous dipropylene glycol solution containing 20% 1,2-benisohtiazolin-3-one)	0.1 % (w/v)
Water		to 1000 ml
Wettable Powder (WP)		
Active Ingredient	Compound of Example 5	80 % (w/w)
Wetting agent	Atlox® 4995 ¹⁾ (polyoxyethylene alkyl ether)	2 % (w/w)
Dispersing agent	Witcosperse® D-60 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkylaryl/polyoxy acetates)	3 % (w/w)
Carrier / Filler	Kaolin	35 % (w/w)
Water Dispersible Granules (WG)		
Active Ingredient	Compound of Example 5	50 % (w/w)

¹⁾ available from ICI Surfactants

²⁾ available from Deutsche Shell AG

³⁾ available from Rhone-Poulenc

⁴⁾ available from Kelco Co.

⁵⁾ available from Zeneca

⁶⁾ available from Witco

EP 1 108 720 A1

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(continued)

Wettable Powder (WP)		
Water Dispersible Granules (WG)		
Dispersing / Binding agent	Witcosperse® D-450 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkyl sulfonates)	8 % (w/w)
Wetting agent Morwet® EFW ⁶⁾	2 % (w/w) (formaldehyde condensation product)	Antifoaming Rhodorsil® EP 6703
3) 1 % (w/w) agent (encapsulated silicone)		
Disintegrant	Agrimer® ATF ⁷⁾ (cross-linked homopolymer of N-vinyl-2-pyrrolidone)	2 % (w/w)
Carrier / Filler	Kaolin	35 % (w/w)

⁶⁾ available from Witco⁷⁾ available from International Specialty Products

[0068] The compositions of this invention can be applied to the plants or their environment simultaneous with or in succession with other active substances. These other active substances can be either fertilizers, agents which donate trace elements or other preparations which influence plant growth. However, they can also be selective herbicides, insecticides, fungicides, bactericides, nematocides, algicides, molluscicides, rodenticides, virucides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, nematodes, fungi and other microorganisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations, if appropriate together with other carrier substances conventionally used in the art of formulation, surfactants or other additives which promote application.

[0069] The active ingredients according to the invention can be employed alone or as formulations in combination with conventional herbicides. Such combinations of at least two herbicides can be included in the formulation or also added in a suitable form with the preparation of the tank mix. For such mixtures at least one of the following known herbicides can be used:

ametrydione, metabenzthiazuron, metamltron, metribuzin, 2,4-D, 2,4-DB, 2,4-DP, alachlor, alloxymid, asulam, atrazin, bensulfu-ron, bentazon, bifenox, bromoxynil, butachlor, chloridazon, chlo-rimuron, chlorpropham, chlorsulfuron, chlortoluron, cinmethylin, clopyralid, cyanazin, cycloate, cycloxydim, dichlobenil, diclo-fop, eptame, ethiozin, fenoxaprop, fluazifop, fluometuron, fluri-done, fluroxypyr, fomesafen, glyphosate, haloxyfop, hexazinone, imazamethabenz, imazapyr, imazaquin, imazethapyr, loxynil, isoproturon, lactofen, MCPA, MCPP, mefenacet, metazachlor, metolachlor, metsulfuron, molinate, norflurazon, oryzalin, oxyfluorfen, pendimethalin, picloram, pretilachlor, propachlor, pyridate, quizalofopethyl, sethoxydim, simetryne, terbutryne, thiobencarb, triallate, trifluralin, diflufenican, propanil, triclopyr, dicamba, desmedipham, acetochlor, fluoroglycofen, halosafen, tral-koxydim, amidosulfuron, cinosulfuron, nicosulfuron, pyrazosulfu-ron, thiameturon, thifensulfuron, triasulfuron, oxasulfuron, azimsulfuron, tribenuron, esprocarb, prosulfocarb, terbutylazin, benfuresate, clomazone, dl-methazone, dithiopyr, isoxaben, quinchlorac, qinmerac, sulfosate, cyclosulfamuron, imazamox, ima-zamethapyr, flamprop-M-methyl, flamprop-M-isopropyl, picolinafen, fluthiamid, isoxaflutole, flurtamone, daimuron, bromobutide, me-thyldimron, dimethenamid, sulcotrione, sulfentrazone, oxadiargyl, acifluorfen, cafenstrole, carfentrazone, diuron, glufosinate.

[0070] Mixtures with other active ingredients like fungicides, insecticides, acaricides and nematocides are possible.

[0071] A suitable concentrated formulation containing a compound according to the invention can, for example, consist of 100 g of active ingredient (compound of formula I), 30 g of dispersing agent, 3 g of antifoaming agent, 2 g of structure agent, 50 g of anti-freezing agent, 0.5 g of a biocidal agent and water ad 1000 ml. Prior to use, it is diluted with water to give the desired concentration of active ingredient.

[0072] For a more clear understanding of the invention, specific examples are set forth below. These examples are merely illustrations and are not to be understood as limiting the scope and underlying principles of the invention in any way. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the following examples and foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

[0073] The structures of the compounds prepared in the following examples were additionally confirmed by NMR and mass spectrometry.

Example 1

[0074] 2-(3-Chloropyridin-5-yloxy)-6-(1-methyl-3-trifluoromethylpyrazol-5-yl)pyridine and 2-(3-chloropyridin-

5-yloxy)-6-(1-methyl-5-trifluoromethylpyrazol-3-yl)pyridine

1A Preparation of 2-chloro-6-acetylpyridine

5 [0075] A solution of 2-chloro-6-cyanopyridine (50g) in THF (400 ml) is cooled to -5 °C and a solution of methylmagnesium iodide in diethyl ether (3 M, 200 ml) is added. After 1 h at 0 °C the ether is distilled off and the THF-mixture is heated to 60 °C for 1 h. The THF is evaporated and the residue is treated with ice water and acidified with 2 M hydrochloric acid. The water phase is extracted with dichloromethane and after drying and evaporation of the organic phase, the residue is purified by silica-gel flash chromatography. The title compound is obtained as an oil (11.2 g).

1B Preparation of 2-chloro-6-(trifluoroacetoacetyl)pyridine

15 [0076] To a mixture of ethyl trifluoroacetate (17.2 g) and sodium hydride (60 % in oil, 5.7 g) in THF (200 ml) is added a solution of 1A (11.2 g) in THF (50 ml) with ethanol (2 drops) and a solution of dibenzo-18-crown-6 (415 mg) in THF (70 ml). The reaction mixture is stirred for 60 h at ambient temperature. After heating for 1 h at reflux temperature, the mixture is acidified with 2M hydrochloric acid and extracted with ethyl acetate. The organic phase is dried and evaporated. One obtains the crude title compound as an oily product (21.5 g).

1C Preparation of 2-chloro-6-(1-methyl-3-trifluoromethylpyrazol-5-yl)pyridine and 2-chloro-6-(1-methyl-5-trifluoromethyl-pyrazol-3-yl)pyridine

25 [0077] A mixture of the crude 1B (9 g) and methylhydrazine (1.9 ml) in ethanol (50 ml) is stirred overnight at ambient temperature. The mixture is heated to reflux for 1 h and evaporated in vacuo. The residue is purified by means of silica-gel flash chromatography. One obtains a mixture of the two title compounds as oil (5.1 g).

1D Preparation of 2-(3-Chloropyridin-5-yloxy)-6-(1-methyl-3-tri-fluoromethylpyrazol-5-yl)pyridine and 2-(3-chloropyridin-5-yloxy)-6-(1-methyl-5-trifluoromethyl-pyrazol-3-yl)pyridine

30 [0078] To a solution of 1C (1.4 g) in sulfolane (5 ml) is added potassium carbonate (1.1 g) and 3-chloro-5-hydroxypyridine (0.71 g). The reaction mixture is heated to 180 °C for 4 h. After cooling, water (100 ml) is added and the mixture is extracted with ethyl acetate:petrol ether (1:1). The organic phase is washed several times with water, dried and evaporated to dryness. After silica-gel flash chromatography, the title compounds are obtained as colorless crystals of mp. 131 °C and 88 °C.

Example 2

[0079] 2-(1-Methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(1-methyl-3-tri-fluoromethylpyrazol-5-yl)pyridine and 2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(1-methyl-5-trifluoromethylpyrazol-3-yl)pyridine

40 [0080] To a solution of 1C (2.6 g) in sulfolane (20 ml) is added potassium carbonate (1.4 g) and the potassium salt of 5-hydroxy-1-methyl-3-trifluoromethylpyrazole (2.0 g). The mixture is heated to 180 °C for 9 h. After cooling, water is added (200 ml) and the mixture is extracted with ethyl acetate. The organic phase is washed several times with water, dried and evaporated to dryness. After silica-gel flash chromatography, the title compounds are obtained as colorless crystals of mp. 108 °C and 71 °C.

Example 3

[0081] 4-Cyano-2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(1-methyl-3-trifluoromethylpyrazol-5-yl)pyridine

50 [0082] A mixture of bis(diphenylphosphino)butane (30 mg) and bis(benzonitrile)dichloropalladium (30 mg) is heated under an inert gas atmosphere in toluene (5 ml) to reflux for 1 h. After cooling, 1-methyl-3-trifluoromethyl-5-tri-n-butyltinpyrazol (0.2 g) and 2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-4-cyano-6-chloropyridine (0.12 g) is added and the mixture is heated to reflux for 3 h. After extractive workup, the residue is purified by silica-gel flash chromatography. One obtains the title compound as colorless crystals of mp. 164-165 °C.

Example 4

55 [0083] 2-(1-Methyl-3-trifluoromethylpyrazol-5-yl)-6-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-5-methylpyrimidine

EP 1 108 720 A1

4A Preparation of 2-Iodo-6-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-5-methylpyrimidine

[0084] To a suspension of 2-amino-4-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-5-methylpyrimidine (5 g) in dimethoxyethane (25 ml) is added isopentyl nitrite (48 ml) and the mixture is heated to 90 °C for 30 min. After cooling, the brownish reaction mixture is evaporated in vacuo and the residue is purified by silica-gel flash chromatography. One obtains the title compound as crystals of mp. 94 °C.

4B Preparation of 1-methyl-3-trifluoromethylpyrazol-5-yl-boronic acid

[0085] A solution of 1-methyl-3-trifluoromethylpyrazol (2 g) in 10 ml THF is cooled under an inert gas atmosphere to -78 °C. A 2 M solution of LDA (9.75 ml) is added dropwise. The mixture is stirred to 10 °C for 1 h and cooled to -75 °C. Trimethylborate (5.8 ml) is added and after stirring for 1 h at -75 °C the mixture is stirred overnight at ambient temperature. The resulting reaction solution is added to 10 % hydrochloric acid (15 ml). The water phase is extracted 3 times with ethyl acetate and the combined organic phases are washed with water and a saturated sodium chloride solution. The organic phase is dried and evaporated and the residue is crystallized from water. After drying, one obtains the title compound as nearly colorless crystals (1.12 g) of mp. 138°C.

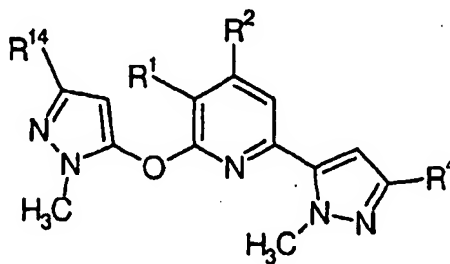
4C Preparation of 2-(1-methyl-3-trifluoromethylpyrazol-5-yl)-6-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-5-methylpyrimidine

[0086] To a solution of 4A (1 g) in toluene (10 ml) is added a 2 M solution of potassium carbonate in water (2.5 ml) under an inert gas atmosphere. A suspension of 4B (0.66 g) and tetrakis(triphenylphosphine)palladium (0.15 g) in methanol (3 ml) is added and the mixture is heated to for 36 h to reflux. After cooling, the organic phase is separated and the water phase is washed twice with ethyl acetate. The combined organic phases are dried, evaporated to dryness and the residue is purified by silica-gel flash chromatography and preparative HPLC. One obtains the title compound as colorless crystals of mp. 113°C.

Examples 5 to 166:

[0087] Further Examples are prepared according to the general method of Example 1 to 4 and are listed in Tables 1 to 4.

Table 1



EP 1 108 720 A1

	Example	R ^{1a}	R ¹	R ²	R ^d	
	5	CF ₃	H	CH ₃	CF ₃	semi-solid
	6	OCF ₃	H	H	CF ₃	
5	7	SCF ₃	H	H	CF ₃	
	8	Cl	H	H	CF ₃	
	9	CF ₃	CH ₃	H	CF ₃	
	10	OCF ₃	CH ₃	H	CF ₃	
	11	SCF ₃	CH ₃	H	CF ₃	
10	12	Cl	CH ₃	H	CF ₃	
	13	OCF ₃	H	CH ₃	CF ₃	
	14	SCF ₃	H	CH ₃	CF ₃	
	15	Cl	H	CH ₃	CF ₃	
15	16	CF ₃	OCH ₃	H	CF ₃	
	17	OCF ₃	OCH ₃	H	CF ₃	
	18	SCF ₃	OCH ₃	H	CF ₃	
	19	Cl	OCH ₃	H	CF ₃	
	20	CF ₃	H	OCH ₃	CF ₃	
20	21	OCF ₃	H	OCH ₃	CF ₃	
	22	SCF ₃	H	OCH ₃	CF ₃	
	23	Cl	H	OCH ₃	CF ₃	
	24	CF ₃	H	H	CClF ₂	
25	25	CF ₃	H	H	C ₂ F ₅	
	26	CF ₃	H	H	Cl	
	27	CF ₃	H	H	OCHF ₂	
	28	CF ₃	CH ₃	H	CClF ₂	
	29	CF ₃	CH ₃	H	C ₂ F ₅	
30	30	CF ₃	CH ₃	H	Cl	
	31	CF ₃	CH ₃	H	OCHF ₂	
	32	CF ₃	H	CH ₃	CClF ₂	
	33	CF ₃	H	CH ₃	C ₂ F ₅	
	34	CF ₃	H	CH ₃	Cl	
35	35	CF ₃	H	CH ₃	OCHF ₂	
	36	CF ₃	OCH ₃	H	CClF ₂	
	37	CF ₃	OCH ₃	H	C ₂ F ₅	
	38	CF ₃	OCH ₃	H	Cl	
40	39	CF ₃	OCH ₃	H	OCHF ₂	
	40	CF ₃	H	OCH ₃	CClF ₂	
	41	CF ₃	H	OCH ₃	C ₂ F ₅	
	42	CF ₃	H	OCH ₃	Cl	
	43	CF ₃	H	OCH ₃	OCHF ₂	
45	44	OCF ₃	H	CH ₃	CClF ₂	
	45	OCF ₃	H	CH ₃	C ₂ F ₅	
	46	OCF ₃	H	CH ₃	Cl	
	47	OCF ₃	H	CH ₃	OCHF ₂	
50	48	Cl	H	CH ₃	CClF ₂	
	49	Cl	H	CH ₃	C ₂ F ₅	
	50	Cl	H	CH ₃	Cl	
	51	Cl	H	CH ₃	OCHF ₂	
	52	SCF ₃	H	CH ₃	CClF ₂	
55	53	SCF ₃	H	CH ₃	C ₂ F ₅	
	54	SCF ₃	H	CH ₃	Cl	

EP 1 108 720 A1

Example	R ¹⁴	R ¹	R ²	R ⁴
55	SCF ₃	H	CH ₃	OCHF ₂
56	CF ₃	H	CN	CClF ₂

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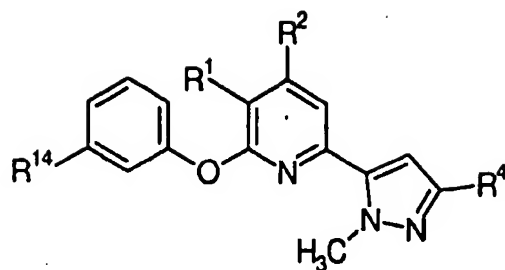
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Table 2



Example	R ¹⁴	R ¹	R ²	R ⁴
56	CF ₃	H	H	CF ₃
57	SCF ₃	H	H	CF ₃
58	Cl	H	H	CF ₃
59	CF ₃	CH ₃	H	CF ₃
60	OCF ₃	CH ₃	H	CF ₃
61	SCF ₃	CH ₃	H	CF ₃
62	Cl	CH ₃	H	CF ₃
63	CF ₃	H	CH ₃	CF ₃
64	SCF ₃	H	CH ₃	CF ₃
65	Cl	H	CH ₃	CF ₃
66	CF ₃	OCH ₃	H	CF ₃
67	OCF ₃	OCH ₃	H	CF ₃
68	SCF ₃	OCH ₃	H	CF ₃
69	Cl	OCH ₃	H	CF ₃
70	CF ₃	H	OCH ₃	CF ₃
71	OCF ₃	H	OCH ₃	CF ₃
72	SCF ₃	H	OCH ₃	CF ₃
73	Cl	H	OCH ₃	CF ₃
74	CF ₃	H	H	CClF ₂
75	CF ₃	H	H	C ₂ F ₅
76	CF ₃	H	H	Cl
77	CF ₃	H	H	OCHF ₂
78	CF ₃	CH ₃	H	CClF ₂
79	CF ₃	CH ₃	H	C ₂ F ₅
80	CF ₃	CH ₃	H	Cl
81	CF ₃	CH ₃	H	OCHF ₂
82	CF ₃	H	CH ₃	CClF ₂
83	CF ₃	H	CH ₃	C ₂ F ₅
84	CF ₃	H	CH ₃	Cl
85	CF ₃	H	CH ₃	OCHF ₂
86	CF ₃	OCH ₃	H	CClF ₂
87	CF ₃	OCH ₃	H	C ₂ F ₅
88	CF ₃	OCH ₃	H	Cl

oil

EP 1 108 720 A1

	Example	R ^{1a}	R ¹	R ²	R ⁴
	89	CF ₃	OCH ₃	H	OCHF ₂
5	90	CF ₃	H	OCH ₃	CClF ₂
	91	CF ₃	H	OCH ₃	C ₂ F ₅
	92	CF ₃	H	OCH ₃	Cl
	93	CF ₃	H	OCH ₃	OCHF ₂
	94	OCF ₃	H	CH ₃	CClF ₂
10	95	OCF ₃	H	CH ₃	C ₂ F ₅
	96	OCF ₃	H	CH ₃	Cl
	97	OCF ₃	H	CH ₃	OCHF ₂
	98	Cl	H	CH ₃	CClF ₂
15	99	Cl	H	CH ₃	C ₂ F ₅
	100	Cl	H	CH ₃	Cl
	101	Cl	H	CH ₃	OCHF ₂
	102	SCF ₃	H	CH ₃	CClF ₂
	103	SCF ₃	H	CH ₃	C ₂ F ₅
20	104	SCF ₃	H	CH ₃	Cl
	105	SCF ₃	H	CH ₃	OCHF ₂
	106	CF ₃	H	CN	CClF ₂

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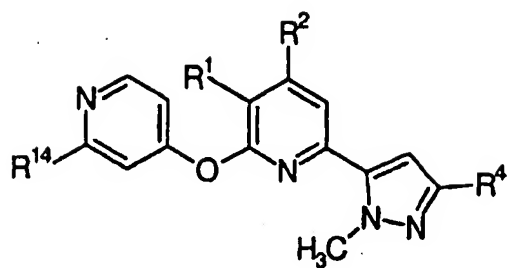
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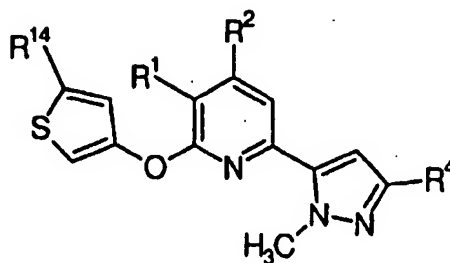
Table 3



Example	R ¹⁴	R ¹	R ²	R ⁴
107	CF ₃	H	H	CF ₃
108	OCHF ₂	H	H	CF ₃
109	Cl	H	H	CF ₃
110	CF ₃	CH ₃	H	CF ₃
111	OCF ₃	CH ₃	H	CF ₃
112	OCHF ₂	CH ₃	H	CF ₃
113	Cl	CH ₃	H	CF ₃
114	CF ₃	H	CH ₃	CF ₃
115	OCHF ₂	H	CH ₃	CF ₃
116	Cl	H	CH ₃	CF ₃
117	CF ₃	OCH ₃	H	CF ₃
118	OCF ₃	OCH ₃	H	CF ₃
119	OCHF ₂	OCH ₃	H	CF ₃
120	Cl	OCH ₃	H	CF ₃
121	CF ₃	H	OCH ₃	CF ₃
122	OCF ₃	H	OCH ₃	CF ₃
123	OCHF ₂	H	OCH ₃	CF ₃

Example	R ¹⁴	R ¹	R ²	R ⁴
124	Cl	H	OCH ₃	CF ₃
125	CF ₃	H	H	CClF ₂
126	CF ₃	H	H	C ₂ F ₅
127	CF ₃	H	H	Cl
128	CF ₃	H	H	OCHF ₂
129	CF ₃	CH ₃	H	CClF ₂
130	CF ₃	CH ₃	H	C ₂ F ₅
131	CF ₃	CH ₃	H	Cl
132	CF ₃	CH ₃	H	OCHF ₂
133	CF ₃	H	CH ₃	CClF ₂
134	CF ₃	H	CH ₃	C ₂ F ₅
135	CF ₃	H	CH ₃	Cl
136	CF ₃	H	CH ₃	OCHF ₂
137	CF ₃	OCH ₃	H	CClF ₂
138	CF ₃	OCH ₃	H	C ₂ F ₅
139	CF ₃	OCH ₃	H	Cl
140	CF ₃	OCH ₃	H	OCHF ₂
141	CF ₃	H	OCH ₃	CClF ₂
142	CF ₃	H	OCH ₃	C ₂ F ₅
143	CF ₃	H	OCH ₃	Cl
144	CF ₃	H	OCH ₃	OCHF ₂
145	OCF ₃	H	CH ₃	CClF ₂
146	OCF ₃	H	CH ₃	C ₂ F ₅
147	OCF ₃	H	CH ₃	Cl
148	OCF ₃	H	CH ₃	OCHF ₂
149	Cl	H	CH ₃	CClF ₂
150	Cl	H	CH ₃	C ₂ F ₅
151	Cl	H	CH ₃	Cl
152	Cl	H	CH ₃	OCHF ₂
153	OCHF ₂	H	CH ₃	CClF ₂
154	OCHF ₂	H	CH ₃	C ₂ F ₅
155	OCHF ₂	H	CH ₃	Cl
156	OCHF ₂	H	CH ₃	OCHF ₂
157	CF ₃	H	CN	CClF ₂

Table 4



EP 1 108 720 A1

Example	R ¹⁴	R ¹	R ²	R ⁴
158	CF ₃	H	H	CF ₃
159	SCF ₃	H	H	CF ₃
160	Cl	H	H	CF ₃
161	CF ₃	CH ₃	H	CF ₃
162	OCF ₃	CH ₃	H	CF ₃
163	SCF ₃	CH ₃	H	CF ₃
164	Cl	CH ₃	H	CF ₃
165	CF ₃	H	CH ₃	CF ₃
166	SCF ₃	H	CH ₃	CF ₃

Herbicidal Activity

[0088] To evaluate their herbicidal activity, compounds according to the invention are tested using a representative range of plants:

- ABUTH *Abutilon theophrasti*
- GALAP *Galium aparine*
- IPOHE *Ipomoea hederacea*
- MATIN *Matricaria inodora*
- STEME *Stellaria media*
- ALOMY *Alopecurus myosuroides*
- ECHCG *Echinochloa crus-galli*
- SETVI *Setaria viridis*
- GLXMA *Glycine max*
- HORVW *Hordeum vulgare*
- TRZAW *Triticum aestivum*
- ZEAMX *zea mays*

1. PRE-EMERGENCE TEST

[0089] The pre-emergence tests involve spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above has recently been sown.

[0090] The soil used in the tests is a prepared horticultural loam. The formulations used in the tests are prepared from solutions of the test compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions are diluted with water and the resulting formulations applied at dosage levels corresponding to 0.025 kg, 0.100 kg or 0.400 kg of active material per hectare in a volume equivalent to 900 litres per hectare. In these tests untreated sown soil are used as controls. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated according to the rating system set forth below:

Rating System	% Difference in Growth Versus Untreated Control
0 - No effect	0
1 - Trace effect	1-5
2 - Slight effect	6-15
3 - Moderate effect	16-29
4 - Injury	30-44
5 - Definite injury	45-64
6 - Herbicidal effect	65-79
7 - Good herbicidal effect	80-90

EP 1 108 720 A1

Rating System System	% Difference In Growth Versus Untreated Control
8 - Approaching complete kill	91-99
9 - Complete kill	100

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[0091] The results of the assessment are set out in Table 5.

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Table 5

Pre-emergence application 3 weeks after treatment

Examp e No.	Dose kg/ha	ABUTH	GALAP	IPOHE	MATIN	STEME	ALOMY	ECHCG	SETVI	GLXMA	HORVM	TRZAW	ZEMMX
3	0.400	8	8	9	9	9	5	4	8	3	5	4	5
	0.100	5	4	2	9	9	3	4	5	1	3	0	3
	0.025	1	1	2	9	8	2	2	3	0	2	0	3
4	0.400	9	8	9	9	9	8	8	9	4	5	4	3
	0.100	7	X	6	8	9	6	7	9	3	4	2	2
	0.025	4	1	4	8	9	2	4	8	2	2	1	2
63	0.400	2	1	3	9	9	5	4	9	0	2	0	0
	0.100	0	0	0	6	3	1	0	5	0	0	0	0
	0.025	X	0	0	X	X	0	0	1	0	0	0	0
X = no value													

2. POST-EMERGENCE TEST

5 [0092] The post-emergence herbicidal activity of the compounds of the present invention is demonstrated by the following test, wherein a variety of monocotyledonous and dicotyledonous plants are treated with formulations prepared from solutions of the test compounds in acetone containing 0.4 % by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions are diluted with water and the resulting formulations applied at dosage levels equivalent of about 0.1 to 0.4 kg per hectare of test compound per pot. After spraying the plants are placed on greenhouse benches and are cared for in the usual manner, commensurate with conventional greenhouse practices. From 2 to 4 weeks after treatment, the seedling plants are examined and rated according to the rating system provided above. The results of the test are set out in Table 6 below.

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Table 6

Post-emergence application 2-4 weeks after treatment

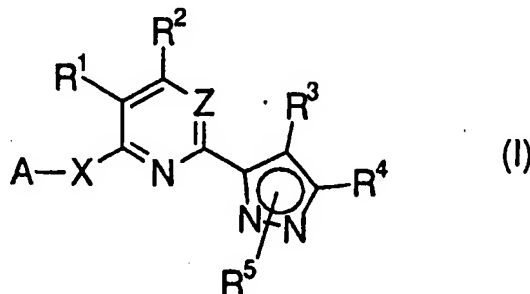
Compound d	Dose kg/ha	ABUTH	GALAP	IPOHE	MATIN	STEME	ALOMY	ECHCG	SETVI	GLXMA	HORVW	TRZAW	ZEAMX
3	0.4	5	9	8	8	-	4	4	7	4	5	4	4
	0.1	4	3	6	8	-	3	4	5	3	3	3	2
4	0.4	7	9	9	7	6	7	8	9	6	5	5	4
	0.1	6	8	9	5	5	5	8	9	4	3	3	2
63	0.4	4	5	8	7	-	2	3	6	7	3	3	3
	0.1	4	5	8	5	-	1	3	3	3	3	3	2

- = not tested

[0093] The compounds of the invention show high selectivity in important crops (soybeans, wheat) at doses required for good weed control in pre- and post-emergence application. They also show good activity, in particular against broadleaf weeds. At the dose of 0.1 kg/ha, which was well tolerated in soybeans and wheat, the compounds of examples 3 and 4 demonstrated good overall levels of weed control.

Claims

1. A compound of the general formula (I)



wherein

A represents an optionally substituted aryl group or an optionally substituted 5- or 6-membered nitrogen- or sulfur-containing heteroaromatic group or a difluorobenzodioxolyl group;

Z represents N or CR⁶;

X represents -O-, -S-, -CH₂O- or -CH₂S-;

R¹ and R² each independently represent a hydrogen or halogen atom, or an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy group, or a haloalkyl, haloalkoxy, cyano, nitro group; or

-S(O)_n-R⁷, in which n is 0, 1 or 2, and R⁷ represents an alkyl or haloalkyl group; or -NR⁸R⁹, in which R⁸ and R⁹ each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group, or R¹⁰O-CY-, in which R¹⁰ represents an alkyl group, and Y represents O or S;

R³ represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, haloalkyl, cyano or nitro group, or -NR¹¹R¹², in which R¹¹ and R¹² each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group,

R⁴ represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy, haloalkyl, haloalkoxy, cyano, nitro group, or -S(O)_m-R¹³, in which m is 0, 1 or 2, and R¹³ represents an alkyl or haloalkyl group; and

R⁵ represents a hydrogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, cycloalkyl, haloalkyl, haloalkenyl, cyanoalkyl or cyano group;

or an agriculturally acceptable salt or N-oxide thereof; with the proviso that

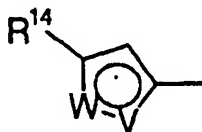
a) R¹ and R⁶ both represent a hydrogen atom, and/or

b) R² represents a halogen atom, or an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy group, or a haloalkyl, haloalkoxy, cyano, nitro group; or -S(O)_n-R⁷, in which n is 0, 1 or 2, and R⁷ represents an alkyl or haloalkyl group; or -NR⁸R⁹, in which R⁸ and R⁹ each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group, or R¹⁰O-CY-, in which R¹⁰ represents an alkyl

group, and Y represents O or S;

In the event that Z represents CR⁶ and A represents an optionally substituted aryl group or an optionally substituted 6-membered nitrogen- or sulfur-containing heteroaromatic group.

2. A compound as claimed in Claim 1, wherein Z represents CR⁶, and A represents an optionally substituted 5-membered nitrogen and/or sulphur containing heteroaromatic group.
3. A compound as claimed in any of Claims 1 to 2, wherein Z represents CR⁶, and R² represents a halogen atom, or an optionally substituted alkyl or alkoxy group, or a cyano group, or -NR⁸R⁹, in which R⁸ and R⁹ each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group.
4. A compound as claimed in any of Claims 1 to 3, wherein A represents a phenyl, pyridyl, pyrazolyl or thienyl group, substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups.
5. A compound as claimed in any of Claims 1 to 4, wherein A is a group of formula

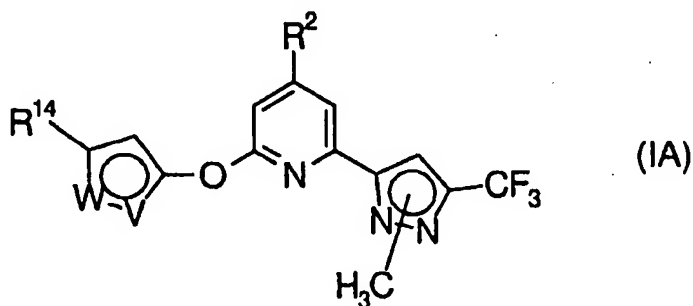


wherein

R¹⁴ represents a halogen atom or a haloalkyl or haloalkoxy group;

W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-N(CH₃)

6. A compound as claimed in any of Claims 1 to 5, wherein R¹⁴ represents a chlorine atom, or a trifluoromethyl, pentafluoroethyl, trifluoromethoxy or difluoromethoxy group.
7. A compound as claimed in any of Claims 1 to 6, wherein R³ represents a hydrogen atom, R⁴ represents a halogen atom, or an alkyl, haloalkyl or haloalkoxy group, and R⁵ represents a hydrogen atom, or an alkyl group.
8. A compound as claimed in any of Claims 1 to 7, wherein X is oxygen.
9. A compound of formula IA



wherein

R² represents a hydrogen atom or an alkyl or cyano group;

R¹⁴ represents a halogen atom or a haloalkyl or haloalkoxy group;

W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-N(CH₃)

10. A compound according to claim 1 selected from the group consisting of

2-(2,4-difluorobenzyloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(2-chloropyrid-4-yloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(3-chloropyrid-5-yloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(3-chloropyrid-5-yloxy)-6-(2'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(2'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-4-methylpyridine,

2-(3-trifluoromethylphenoxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-4-methylpyridine,

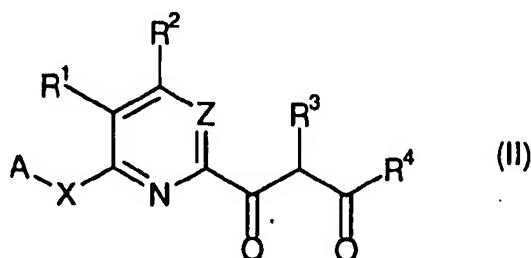
2-(benzyloxy)-4-cyano-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

4-cyano-2-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-6-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-pyridine,

4-(1-methyl-3-trifluoromethylpyrazol-5-yl-oxy)-2-(1'-methyl-3'-trifluoromethylpyrazol-5'-yl)-5-methyl-pyrimidine.

11. A process for the preparation of a compound of general formula I as defined in claim 1, which comprises

(a) reacting a respective compound of the general formula II,



In which A, R¹, R², R³, R⁴, X and Z have the same meaning as in formula I, with hydrazine to obtain a compound of formula I, wherein R⁵ represents a hydrogen atom, and

(b) reacting the resulting compound with a compound of formula III,

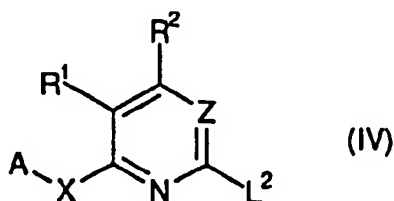


In which R⁵ has the same meaning as in Formula I, and

L¹ represents a suitable leaving group,

optionally in the presence of a base.

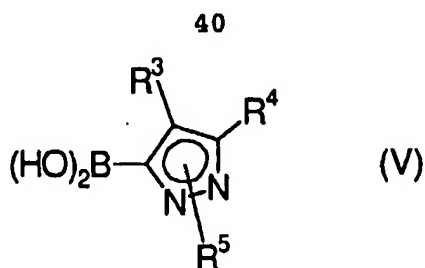
12. A process for the preparation of a compound of general formula I as defined in claim 1, which comprises reacting a respective compound of the general formula IV,



In which

A, R¹, R², X and Z have the same meaning as in formula I, and

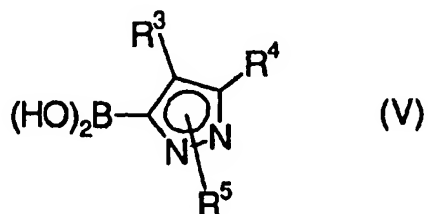
L¹ represents a suitable leaving group,
with a pyrazol-5-ylboronic acid of formula V



In which

R³, R⁴ and R⁵ have the same meaning as in Formula I, in the presence of a transition metal and optionally a base.

13. A pyrazol-5-ylboronic acid of formula V



In which

R³ represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, haloalkyl, cyano or nitro

EP 1 108 720 A1

group, or $-NR^{11}R^{12}$, in which R^{11} and R^{12} each independently represent a hydrogen atom, an alkyl, alkenyl, aralkyl or aryl group,

R^4 represents a hydrogen or halogen atom, or an alkyl, alkenyl, alkynyl, alkoxy, alkoxyalkyl, alkoxyalkoxy, haloalkyl, haloalkoxy, cyano, nitro group, or $-S(O)_m-R^{13}$, in which m is 0, 1 or 2, and R^{13} represents an alkyl or haloalkyl group; and

R^5 represents a hydrogen atom, or an alkyl, alkenyl, alkynyl, alkoxyalkyl, cycloalkyl, haloalkyl, haloalkenyl, cyanoalkyl or cyano group;

14. A herbicidal composition comprising at least one compound of general formula I, as claimed in Claim 1, together with an agronomically acceptable carrier.
15. A composition as claimed in Claim 13, comprising at least two carriers, at least one of which is a surface-active agent.
16. A method of combating undesired plant growth at a locus, comprising application to the locus of a herbicidally effective amount of a compound of general formula I, as claimed in Claim 1.



European Patent
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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 69 12 6776 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	WO 98 21199 A (CIBA GEIGY AG ; SCHURTER ROLF (CH); NEBEL KURT (CH); BRUNNER HANS G) 22 May 1998 (1998-05-22) * page 131; claim 1; example 477 * * page 88; example 502 * * page 89; example 536 * * page 72; examples 34,35 * * page 153; example 031 * ---	1-11, 14-16	C07D401/04 C07D403/14 C07D401/14 A01N43/56
D,X	WO 98 56789 A (SELBY THOMAS PAUL ; DU PONT (US)) 17 December 1998 (1998-12-17) * page 121; example 7 * * scheme 1 on page 7 * ---	1-16	
D,X	WO 99 59990 A (NOVARTIS ERFINDE VERWALT GMBH ; NOVARTIS AG (CH); NEBEL KURT (CH); M) 25 November 1999 (1999-11-25) * examples 315,407,408; table A * ---	1-10, 14-16	
A	EP 0 361 114 A (NIHON NOHYAKU CO LTD) 4 April 1990 (1990-04-04) * examples 22,120,173; table 1 * ---	1-10, 14-16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07D A01N
<p>INCOMPLETE SEARCH</p> <p>The Search Division considers that the present application, or one or more of its claims, does not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely: 10, 13</p> <p>Claims searched incompletely: 1-9,11,12,14-16</p> <p>Claims not searched:</p> <p>Reason for the limitation of the search:</p> <p>The meaning of the residue R6 as indicated in group 2 of the formula I has neither been defined in the claims nor in the description. The search has thus been limited to the individualized embodiment of R6, which is R6 = hydrogen.</p>			
Place of search MUNICH		Date of completion of the search 4 April 2001	Examiner Härtinger, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

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